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Information is provided regarding the nature, magnitude, and extent of the emissions of barium in the United States for the year 1969. Background information concerning the basic characteristics of the barium (barite) industry has been assembled and included. Brief process descriptions are given; they are limited to the areas that are closely related to existing or potential atmospheric losses of the pollutant. The barium emissions and emission factors are based on data obtained from production and reprocessing companies. Additional information was acquired during field trips to inspect the air pollution control equipment and observe processing operations. Emissions to the atmosphere during the year were 15,420 tons. Nearly 18 percent of the emissions resulted from the processing of barite, more than 28 percent from the production of chemicals, 23 percent from the manufacture of various end products, and about 26 percent from the combustion of coal. The wear of rubber tires was a relatively minor emission source.

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REPORT

NATIONAL INVENTORY OF SOURCES AND EMISSIONS BARIUM, BORON, COPPER, SELENIUM, AND ZINC

1969

for

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF AIR PROGRAMS
CONTRACT NO. 68-02-0100

BARIUM

SECTION I

by

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May 1972

PREFACE

This report was prepared by W. E. Davis & Associates pursuant to Contract No. 68-02-0100 with the Environmental Protection Agency, Office of Air Programs.

The inventory of atmospheric emissions has been prepared to provide reliable information regarding the nature, magnitude, and extent of the emissions of barium in the United States for the year 1969.

Background information concerning the basic characteristics of the barium (barite) industry has been assembled and included. Process descriptions are given, but they are brief, and are limited to the areas that are closely related to existing or potential atmospheric losses of the pollutant.

Due to the limitation of time and funds allotted for the study, the plan was to personally contact all of the mining and producing companies and about twenty percent of those in each major emission source group to obtain the required information. It was known that published data concerning the atmospheric emissions of barium were virtually nonexistent, and contacts with industry ascertained that atmospheric emissions were not a matter of record. The barium emissions and

emission factors that are presented are based on the summation of data obtained from production and reprocessing companies. Additional information was acquired during field trips to inspect the air pollution control equipment and observe processing operations.

ACKNOWLEDGEMENTS

This was an industry oriented study and the authors express their appreciation to the many companies and individuals in the barium (barite) industry for their contributions.

We wish to express our gratitude for the assistance of the various societies and associations, and to the many branches of the Federal and State Governments.

Our express thanks to Mr. C. V. Spangler, Project Officer, EPA, Office of Air Programs, Research Triangle Park, N. C., for his helpful guidance.

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SUMMARY

The flow of barium in the United States has been traced and charted for the year 1969 (Figure I). The consumption was 934,000 tons, while domestic production totaled 603,000 tons. Imports and exports were 344,000 and 10,000 tons, respectively.

Emissions to the atmosphere during the year were 15,420 tons (Table I). Nearly 18 percent of the emissions resulted from the processing of barite, more than 28 percent from the production of chemicals, 23 percent from the manufacture of various end products, and about 26 percent from the combustion of coal. The wear of rubber tires was a relatively minor emission source.

Emission estimates for processing, chemical production, and the manufacture of end use products are based on unpublished data obtained from industrial sources.

TABLE I

EMISSIONS BY SOURCE
1969

Source Category	Source Group	Emissions - Tons		Emissions %
Mining			30	--
Processing			2,700	17.5
Chemical Production			4,400	28.5
End Product Uses			4,240	27.5
	Well Drilling Mud	70		
	Glass	40		
	Paint	30		
	Rubber	600		
	Miscellaneous	3,500		
Other Emission Sources			4,050	26.5
	Coal	4,000		
	Cast Iron	50		
TOTAL			15,420	100.0

TABLE II

EMISSIONS BY REGIONS

	Tons
Region No. 1	5,170
Region No. 2	5,260
Region No. 3	3,870
Region No. 4	1,120
TOTAL	15,420

Region No. 1

Arizona
California
Colorado
Idaho
Montana
Nevada
New Mexico
Oregon
Utah
Washington
Wyoming

Region No. 2

Illinois
Indiana
Iowa
Kansas
Michigan
Minnesota
Missouri
Nebraska
North Dakota
Ohio
South Dakota
Wisconsin

Region No. 3

Alabama
Arkansas
Delaware
Florida
Georgia
Kentucky
Louisiana
Maryland
Mississippi
North Carolina
Oklahoma
South Carolina
Tennessee
Texas
Virginia
West Virginia
District of Columbia

Region No. 4

Connecticut
Maine
Massachusetts
New Hampshire
New Jersey
New York
Pennsylvania
Rhode Island
Vermont

EMISSION FACTORS

The emission factors presented herein are the best currently available. They were determined through a combination of methods consisting of: (1) direct observation of emission data and other related plant processing and engineering data; (2) estimates based on information obtained from literature, plant operators, and others knowledgeable in the field; (3) calculations based on experience and personal knowledge of metallurgical processing operations; and (4) specific analytical results where available.

The basic data used to calculate the emission factors are contained in the files of the Contractor.

TABLE III

EMISSION FACTORS

Mining	100 lb/1,000 tons barite mined
Processing	5 lb/ton barite processed
Barium Chemicals	50 lb/ton barite processed
End Product Uses of Barium	
Oil and Gas Well Drilling	110 lb/1,000 tons barite used
Glass Manufacture	2 lb/ton barium processed
Paint Manufacture	2 lb/ton barium processed
Rubber Tire Wear	0.3 lb/million miles
Other Emission Sources	
Coal	15 lb/1,000 tons of coal burned
Cast Iron	5 lb/1,000 tons of process weight

MINERAL SOURCES OF BARIUM

Barium (Ba) is a relatively soft, silver white metal that occurs in nature only in combination with other elements. It is found in small quantities in most igneous rocks; however, the only minerals that are commercially important are barite ($BaSO_4$) and witherite ($BaCO_3$). These minerals are mined almost entirely for the production of barium compounds.

Barite is widely distributed. It occurs in large deposits in many parts of the world, including several areas in the United States. The most important barite-producing countries are the United States, West Germany, U. S. S. R., Mexico, Italy, Greece, Iceland, Canada, and China. In the United States the leading producer during 1969 was Nevada, supplying 30 percent of the total. Missouri produced 28 percent; Arkansas, 20 percent; Georgia, 12 percent; and Alaska, California, North Carolina, and Tennessee accounted for the remaining 10 percent.

The world reserves of the mineral witherite are limited. It is found only in small quantities in the United States and is not mined commercially in this country. The only commercial

production in the world comes from a mine in Northumberland, England.

Domestic sources of barium, other than barite, have been investigated and reported by the Bureau of Mines, the U. S. Geological Survey, and others. These reports indicate some barium is found in coal, feldspar, and mica.

MATERIAL FLOW THROUGH THE ECONOMY

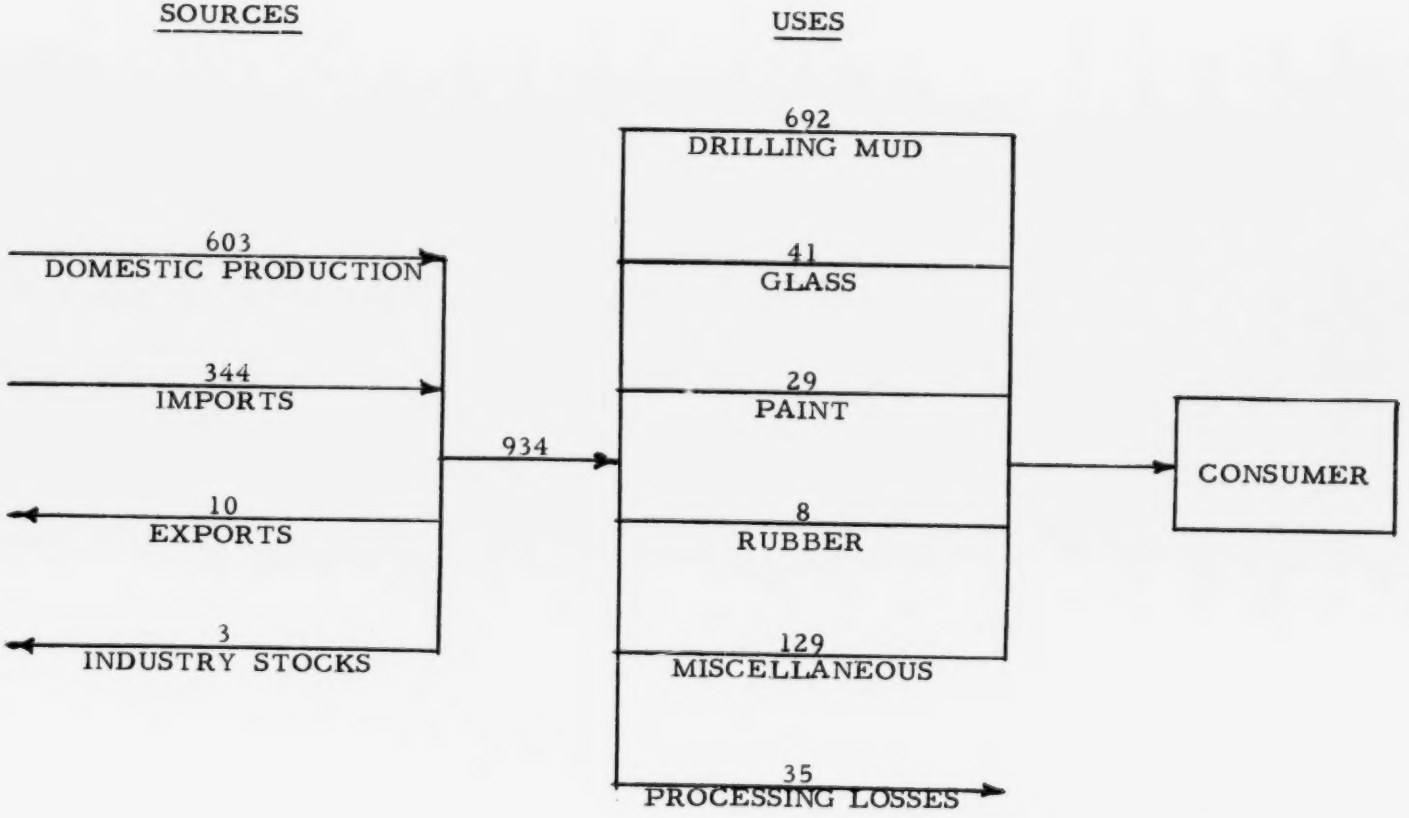
The sources and uses of barium in the United States during 1969 are shown in Figure I. The domestic production totaling 603,000 tons was about 64 percent of the quantity consumed and the remainder that was needed was imported principally from Mexico, Ireland, Canada, Peru, Italy, Greece, and Morocco.

The most important application of barium during 1969 was in oil and gas well drilling muds. About 74 percent was used for this purpose as a weighting agent, barite being suitable because of its chemical inertness, high density, and low cost. A significant amount of barium (14 percent) was used for miscellaneous purposes in the electronic, ceramic, and plastic industries; also in ink fillers, green fire, oils and greases, beet sugar refining, and water treatment. Other categories employing barium were glass (4 percent), paint (3 percent), and rubber (one percent).

BARIUM

MATERIAL FLOW THROUGH THE ECONOMY - 1969

(Thousand Tons)



Data source - U. S. Bureau of Mines.

Figure I

USES AND EMISSIONS OF BARIUM

MINING

During 1969 about 89 percent of the barite was produced in the states of Nevada, Missouri, Arkansas, and Georgia. It was mined both by open-pit and underground methods, and the operations performed at the different mine sites varied somewhat principally because of the type of ore mined.

In Nevada the ore is high-grade and processing is relatively simple in order to prepare it for use as oil well drilling mud. Typically, it is mined, crushed, and screened at the mine site. The fines that are discarded contain 70 to 75 percent barium sulfate, while the ore shipped to the mill contains about 92 percent. On the other hand, the barite ore currently mined in Arkansas is approximately 50 percent barium sulfate and processing operations at or near the mines are more complex.

In Missouri the situation is entirely different. The barite is mined or removed from residual deposits which are about 90 percent clay. Operations at the mines include removal of the clay from the barite using log washers with the fine

barite in the overflow recovered by tabling and froth flotation. Residual deposits also occur in Georgia, Tennessee, and several eastern states.

From the standpoint of emissions to the atmosphere, the principal losses that occur at barite mine sites are those that are due to blasting, ore handling, crushing, loading, and hauling. At one mining location which is typical of many others, the ore loosened by blasting is loaded on trucks for transport to the crusher. The road used is graveled with discarded barite ore and considerable dust is created by movement of the trucks.

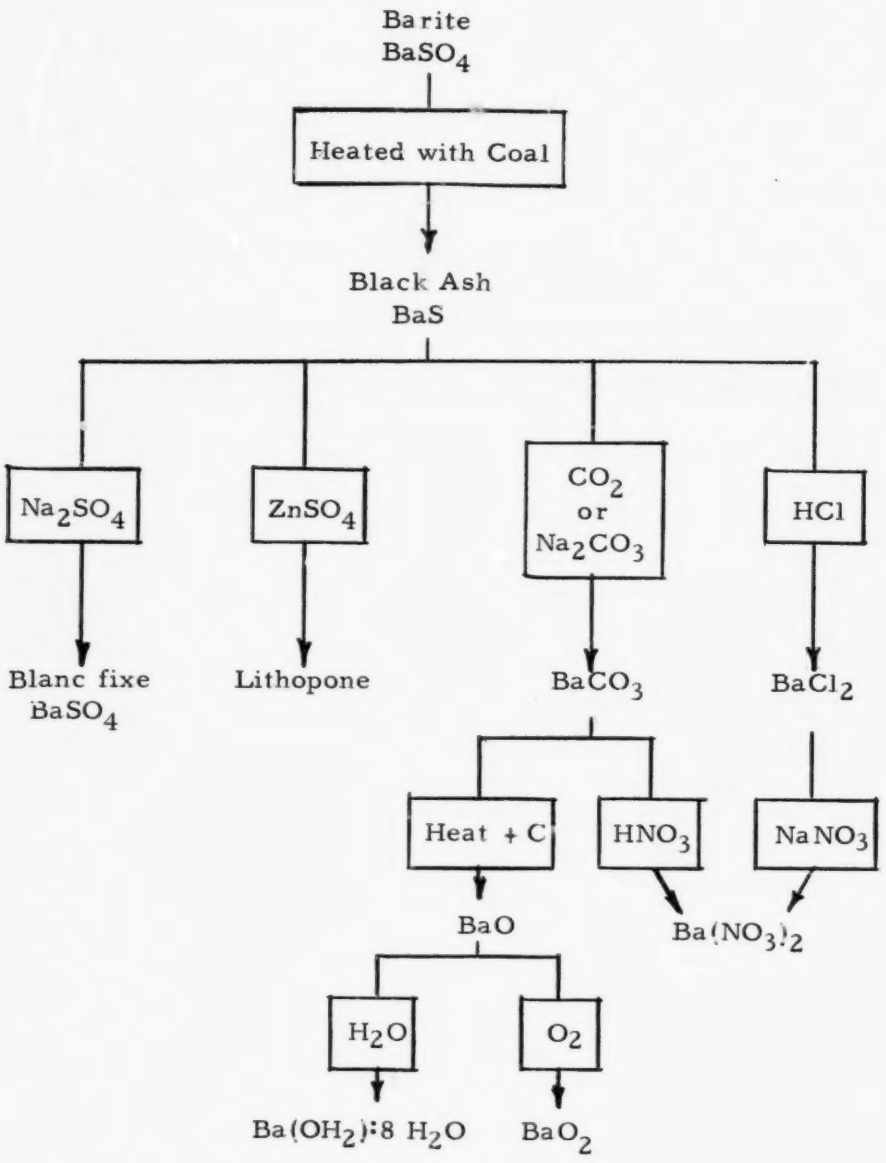
During this study 6 barite mines were visited in Arkansas and Nevada, but records concerning emissions were not available. Based on site inspections, the Contractor's estimate of barium emissions to the atmosphere from sources of mining is 100 pounds per thousand tons of barite ore mined. Barium emissions to the atmosphere during 1969 totaled approximately 30 tons.

PROCESSING

Barite, sometimes referred to as barytes, heavy spar, or tiff, is processed in several different ways depending upon the purity of the ore mined and the use intended for the end product. Currently the ore produced in Nevada is relatively pure (about 80 to 85 percent $BaSO_4$) and it may be processed in a dry condition, whereas the ore now mined in Arkansas contains considerably less barium sulfate and must be upgraded by flotation. In Missouri and Georgia the clay must be washed away from the barite, which is otherwise relatively pure.

Commercially 4 classifications of barite are commonly used. Crude barite is the raw material for producing barium sulfide (BaS), commonly called black ash, which is a compound from which many other useful chemicals are produced as shown in Figure II. Coarsely ground barite (20 mesh) is a form preferred by the glass industry. It is added to the mix to lower the melting point of the glass melt. Finely ground (minus 325 mesh) is the product for which there is the greatest demand. It is used as a weighting agent in oil and gas well drilling mud. Finely ground (bleached and treated) is a refined product suitable as a filler for paints.

BARIUM COMPOUNDS PRODUCED FROM BARITE



Kirk, R. E. and Othmer, D. F.; Encyclopedia of Chemical Technology - Vol. 3, 2nd rev. ed. John Wiley & Sons, Inc.; New York, N. Y.; 1968 p. 82.

Figure II

In Nevada the ore is usually crushed and screened at the mine, then hauled to the mill where it is crushed again prior to pulverizing in a ball or Raymond mill. Most of the product is for use in oil well drilling muds and is shipped in bags or in bulk by railroad or truck. At one of the 4 locations inspected in Nevada during this study, large quantities of dust were observed as the ore was dumped from trucks at the mill. The open conveyor system from the stockpile to the processing plant was also a source of barium sulfate emissions. One cyclone collector was the only air pollution control equipment in service and it was obviously not an effective installation. At another plant the ore was only crushed and screened prior to shipment to another processing location. There was no air pollution control equipment.

At one of the 3 milling operations inspected in Arkansas, the ore received by trucks from the mine was dumped into a crusher bin before entering the crusher where it was mixed with water. The next operations consisting of wet grinding and flotation were followed by drying prior to preparation of the product for shipment. There were some emissions to the atmosphere as the ore was dumped from the trucks and during drying. Even though a water spray was used in the

exhaust stack of the dryer, the emissions were quite noticeable. At this plant about 80 percent of the product is bulk loaded and shipped in closed hopper cars. The remaining 20 percent is bagged in the shipping department where bag filters are employed to control the emissions. Inspections at the other 2 plants revealed that dust collection systems are used that include both cyclones and bag filters. Generally, the inspections indicated that the degree of emission control was about the same at all 3 mills in Arkansas.

Processing operations in Missouri and Georgia are similar, consisting of washing followed by drying, milling, and shipping. The principal sources of emissions to the atmosphere are drying, milling, and materials handling. Air pollution control equipment installed includes cyclone collectors and bag filters. Drying temperature is controlled to protect the filter bags and this effectively prevents chemical conversion of the barite. Particulate emissions are reported to be $BaSO_4$ minus 325 mesh, probably averaging less than 4 microns.

While this study was in progress 13 companies were contacted regarding the production of crude and ground barite. The emission data furnished by one company was essentially

complete, and that from 4 others contained some information concerning various parts of the processing plants. The data obtained from industry indicate that barium emissions to the atmosphere due to the milling of barite ore range from 2 to 8 pounds per ton of barite produced. The emissions are principally in the form of barium sulfate dust, with the particle size in the range of one to 10 microns [1].

Based on 1,077,000 tons of barite production during 1969 [2] and average emissions of 5 pounds of barium per ton of barite produced, the barium emissions in the United Stated totaled nearly 2,700 tons.

1- Private communication.

2- Minerals Yearbook; Bureau of Mines; 1969.

PRODUCTION OF METALLIC BARIUM

Metallic barium may be produced either by carbon reduction or by electrolysis; however, direct reduction methods have almost entirely supplanted fused-salt electrolysis. The most effective process is one which reduces barium oxide with a suitable nonreactive, nonvolatile element such as silicon or aluminum.

One method of conducting the basic reaction is as follows. Barium oxide and aluminum powder are briquetted and placed in a horizontal metal retort, which is heated to 2,000 or 2,200 F for about 8 hours at a pressure of about 0.1 millimeters of mercury. A water-cooled condenser fixed at one end of the retort is used to condense the barium vapor.

At present only a small amount of metal is produced for use in alloys and as a "getter" to remove the final traces of gas from electron tubes during their manufacture. Nevertheless, there is a large potential market provided the cost of the metal could be reduced substantially. Due to limited metal production during 1969, barium emissions were negligible.

PRODUCTION OF BARIUM CHEMICALS

In the United States all major barium chemicals are produced using barite as the raw material for the manufacture of barium sulfide, BaS, also known as black ash. Subsequently, the black ash is the raw material for producing barium carbonate, $BaCO_3$; barium chloride, $BaCl_2$; blanc fixe, $BaSO_4$; and other barium compounds. In turn barium carbonate may be used to make barium oxide, BaO; barium hydroxide, $Ba(OH)_2$; and barium nitrate, $Ba(NO_3)_2$.

To make black ash, the barite is ground to about 20 mesh and mixed with coal of 1/2 inch size, approximately 5 parts barite to one part coal, then reduced at high temperature to barium sulfide (Figure III). There are 2 major types of reducing furnaces, the batch rotary and the continuous process. Batch rotary furnaces are brick lined, fired with gas, oil, or coal, and normally charged through a side door. In about 3 hours after the fire is started, as the temperature approaches 2,100 to 2,200 F, the charge becomes slightly sticky. At this point reduction is practically complete, the fire is turned off, and the charge is dumped. In the continuous process, the feed is at the rear of the furnace with

BARIUM SULFIDE PRODUCED FROM BARITE

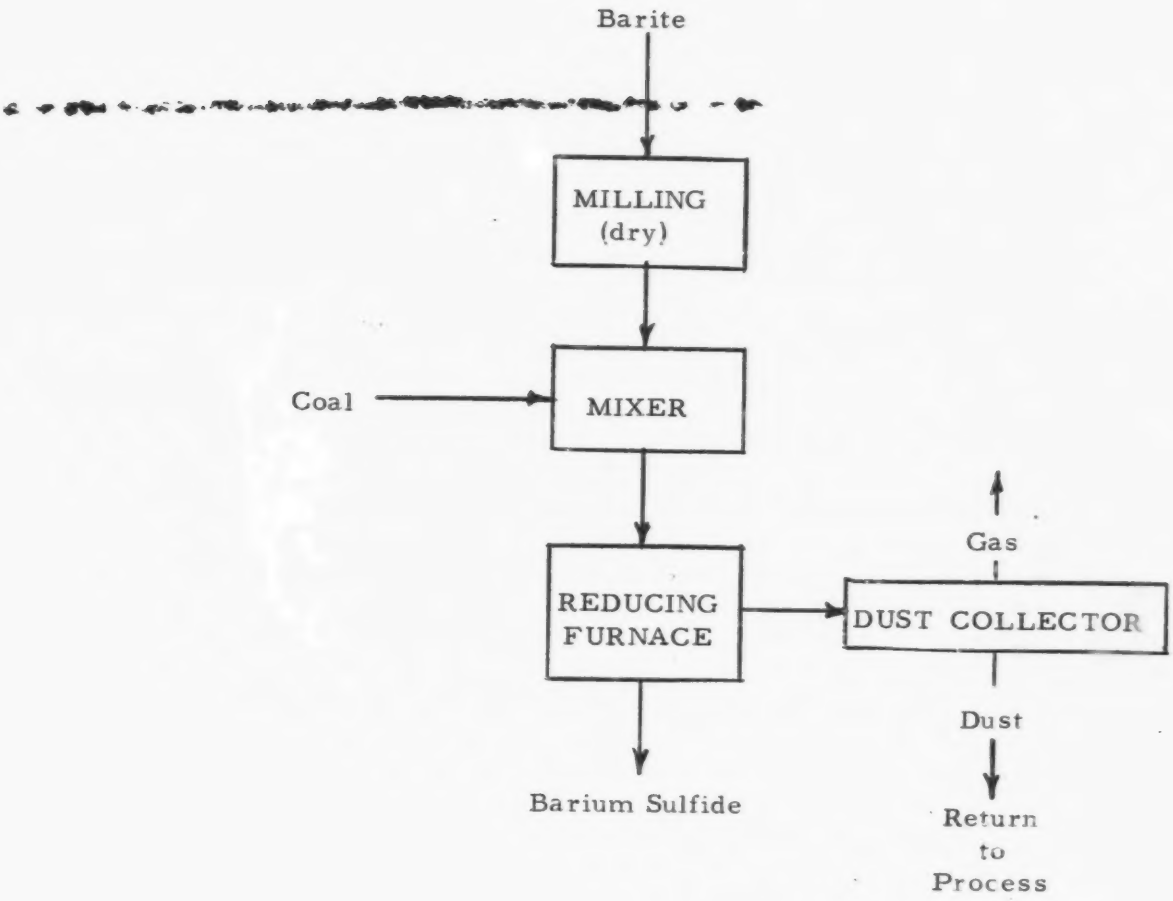


Figure III

heat applied countercurrent to the flow of coal (or coke). Barite and black ash are discharged at the front of the long kiln.

If the black ash is used in the same plant to produce barium carbonate, it is conveyed to a grinding and dissolving plant where it is ground in a wet ball mill or a hammer mill before it is separated from the insoluble gangue by hot water leaching.

There are 2 basic methods for producing barium carbonate. One method is to react black ash with sodium carbonate followed by precipitation, washing, dewatering, drying, and grinding (Figure IV). The other method is a straight gassing process using carbon dioxide to react with the black ash.

Barium chloride is another chemical produced from black ash. A barium sulfide solution is treated with hydrochloric acid in a rubber-lined agitated reaction vessel that is equipped with a gas outlet pipe to carry away the hydrogen sulfide generated during processing. The resulting barium chloride liquor is concentrated by evaporation and crystallization, and the hydrogen sulfide is normally burned to sulfur dioxide in a flare stack.

BARIUM CARBONATE PRODUCED FROM BARIUM SULFIDE

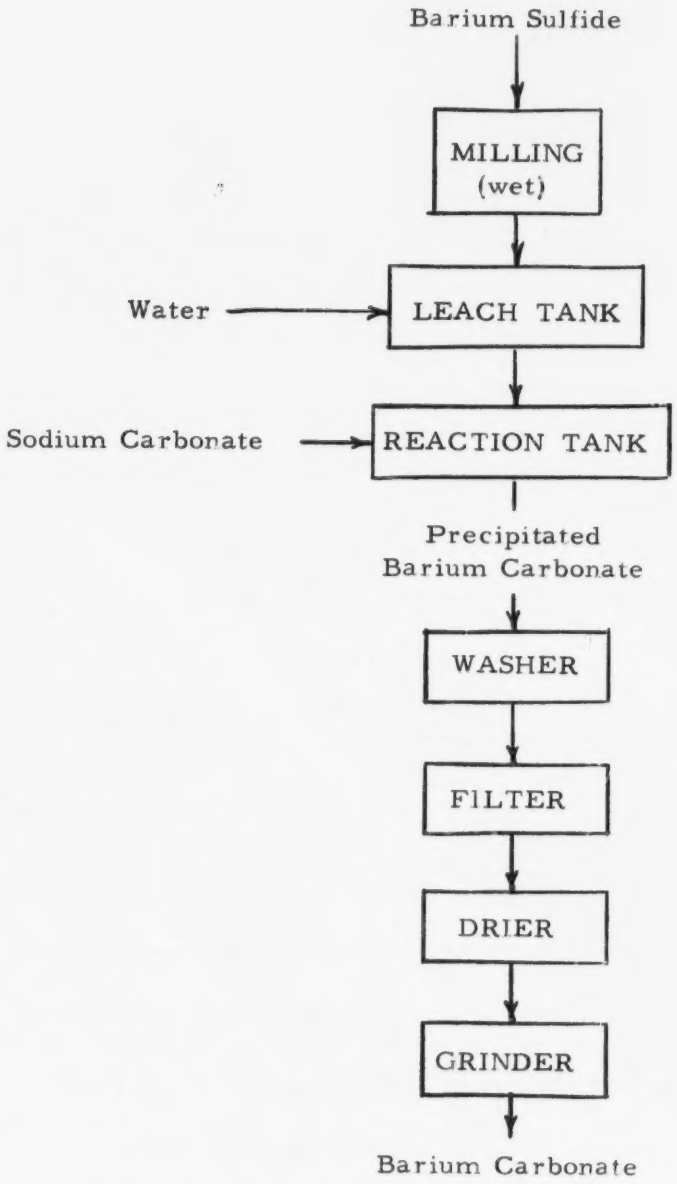


Figure IV

Blanc fixe, used principally as a pigment extender, is a pure form of barium sulfate. Its preparation is quite similar to that of barium carbonate, except that sodium sulfate is used instead of sodium carbonate.

The steps in the manufacture of barium oxide and barium hydroxide are shown in Figure V. Using barium carbonate as the raw material, the oxide may be prepared by dissociating the carbonate at high temperatures after mixing with carbon in some form such as coke or carbon black. The hydroxide is produced by dissolving the oxide in hot water, filtering the insoluble material, and separating the hydrated crystal in a crystallizer. Dewatering, drying, and packaging are the final processing steps. An alternate method for making the hydroxide is to start with black ash as the raw material and use a catalyst to produce the hydroxide directly.

Lithopone is used extensively in rubber, paint, and numerous other products. It is manufactured by adding a solution of zinc sulfate to barium sulfide leach liquor. The resulting mixture is then filtered, washed, dried, calcined under controlled conditions, milled, and packaged for shipment.

Many other barium chemicals produced in smaller quantities

BARIUM HYDROXIDE PRODUCED FROM BARIUM CARBONATE

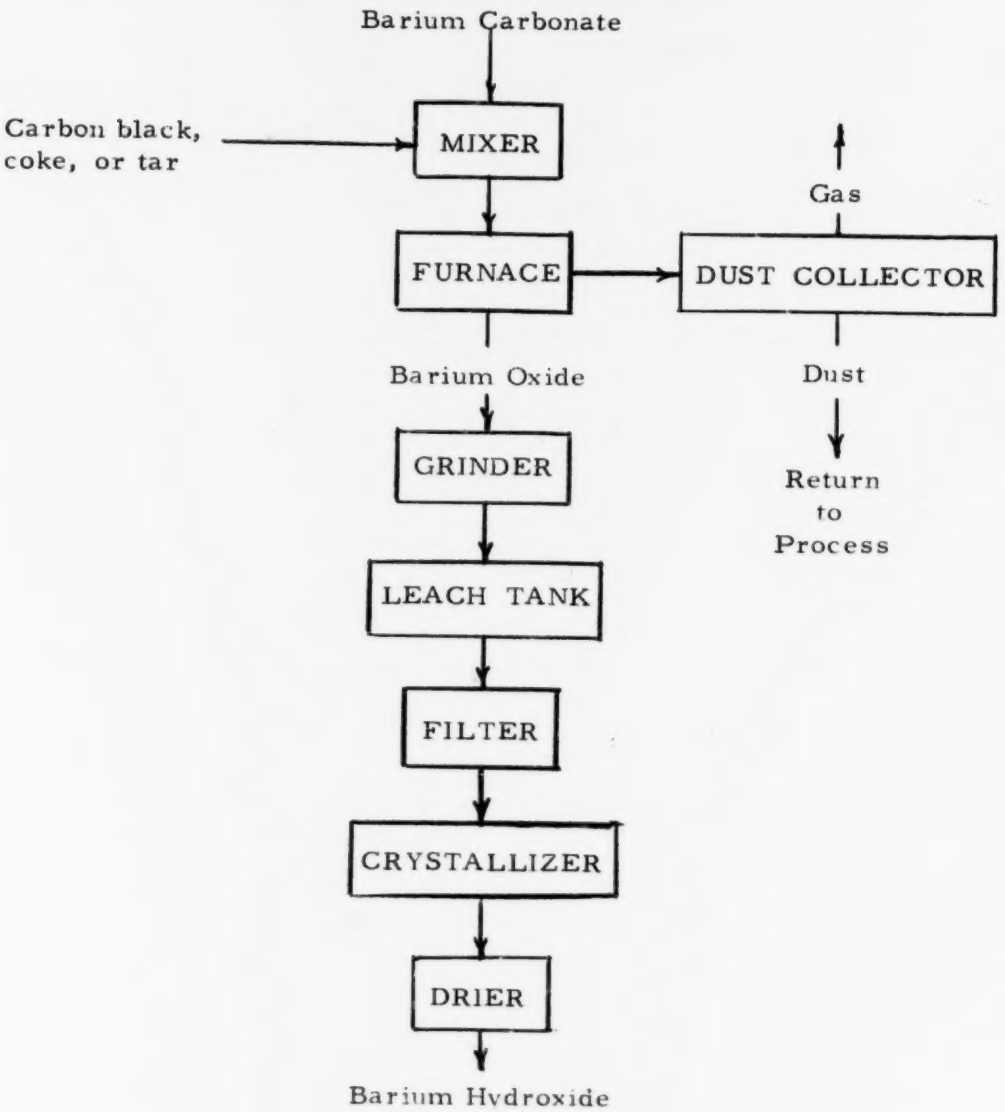


Figure V

include barium ferrite used in magnets for electrical devices; barium silicate and barium stearate which are ingredients in stabilizers for polyvinyl chloride; barium titanate and barium zirconate that are employed in the manufacture of various electronic articles. These compounds have gained popularity during recent years and their importance may increase in the future. Figure VI is a flow diagram showing the principal steps in preparing barium stearate. The procedures are somewhat the same for barium silicate, except the raw material is barium chloride and it is reacted with sodium silicate gel.

The manufacture of barium titanate and barium zirconate are also similar. Barium carbonate is dry mixed with titanium dioxide or zirconium oxide after which the mix is calcined, milled, dewatered, dried, and pulverized.

From the standpoint of emissions to the atmosphere, the production of black ash is the most important barium chemical. The emissions that occur during unloading, stockpiling, materials handling, grinding, mixing, and reducing are reported to be barite and barium sulfide with the size of most particles less than 5 microns. In general the air pollution control equipment consists of settling chambers and cyclone

BARIUM STEARATE PRODUCED FROM BARIUM HYDROXIDE

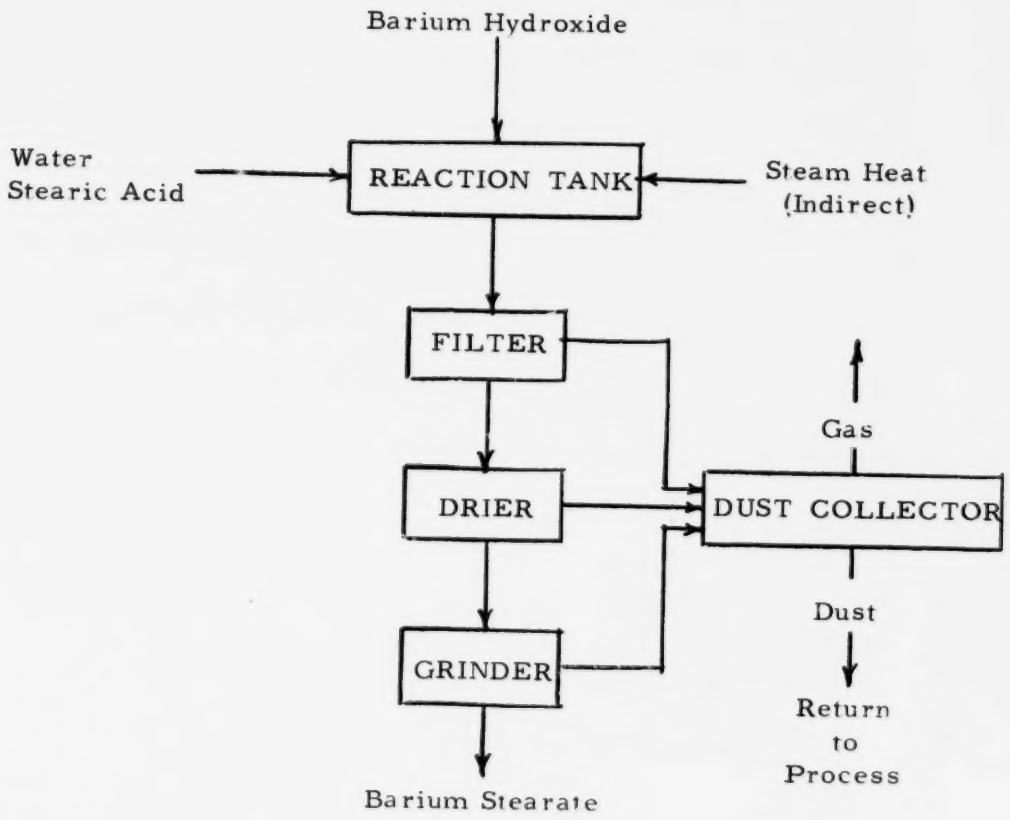


Figure VI

collectors; however, at one plant that was inspected part of the fine gas from the reducing furnace was cleaned in water scrubbers so that it could be used as the carbon dioxide source for the barium carbonate unit.

Other barium chemical processes that have been described are also troubled with emissions to the atmosphere, but to a somewhat lesser extent. Materials handling, grinding, mixing, calcining, and drying are the operations that account for most of the particulate discharge. In many instances materials handling, mixing, and grinding emissions are uncontrolled.

Estimates of emissions were obtained from 4 major producers of barium compounds; however, it was evident that most of the data was for certain production units and did not include plant emissions from all sources. Generally, the only emission estimates were those concerning controlled sources.

Based on the estimates from industry and the information obtained during plant inspections, barium emissions to the atmosphere from sources of chemical production are estimated by the Contractor at 50 pounds per ton of barite processed. The ground and crushed barite used for chemicals during

1969 has been reported by the Bureau of Mines as 177,570 tons [1]; therefore, the barium emissions to the atmosphere during the year totaled 4,400 tons.

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1. Minerals Yearbook, Bureau of Mines, 1969.

END PRODUCT USES OF BARIUM

Manufacturers in all industries were contacted during this study concerning materials handling, manufacturing operations, pollution control equipment, and emissions to the atmosphere as related to the production and use of barium and barium compounds. The information obtained indicates that barium emissions are negligible except in those manufacturing operations and end product uses that are described herein.

Oil and Gas Well Drilling Mud

The major use for barium is as a weighting agent in oil and gas well drilling muds. For this purpose it is used in the form of barite containing about 92 percent or more barium sulfate. The principal requirements are chemical inertness, high density, fineness, and low cost. Some iron oxide and other impurities are not objectionable as long as the barite meets these requirements and has a specific gravity of at least 4.2.

Drilling muds serve several purposes. They help lubricate and cool the drilling bit, plaster the walls of the drill hole to prevent caving, carry the cuttings up to the ground surface,

and restrain high pressure thus preventing blowouts. In rotary drilling the bit is rotated by means of a hollow shaft and the mud is pumped downward inside the shaft removing cuttings as they are formed and carrying them upward in the annular space between the shaft and the wall of the drill hole.

The barite prepared for use in drilling mud is ground to 95 percent minus 325 mesh at the mill and shipped in bags or in bulk. Atmospheric emissions at the well drilling sites are those associated with unloading and handling the material. There were no atmospheric emission records available from those contacted about the use of barite in drilling mud; therefore, the Contractor's estimate of 110 pounds of barium emissions per thousand tons of barite is based on observations of material handling emission problems at shipping points.

During 1969 about 1,240,000 tons of barite (692,000 tons barium content) were used in well drilling muds; therefore, barium emissions to the atmosphere totaled about 70 tons.

Glass

The second most important use of barium is in the manufacture of glass. It is used for several specific purposes

in the form of barite, barium carbonate, barium nitrate, barium hydroxide, and barium oxide. It fluxes the heat insulating froth that forms on the melt surface, thereby effecting a saving in fuel. It acts as an oxidizer and decolorizer. It also makes the glass easier to work and increases its brilliance.

Glass manufacturers usually prefer barite with a maximum of 1.5 percent silicon dioxide, 0.15 percent aluminum oxide, and 0.15 percent iron oxide, as well as a minimum of 98 percent barium sulfate. The preferred particle size ranges from 30 to 140 mesh.

Raw materials for glass manufacture are shipped in packages or in bulk. Unloading may be accomplished by manual labor, vibrator-gravity, drag shovels, or vacuum systems. Methods of material storage vary widely, but in a large installation the raw materials for the glass mix are often stored in gravity feed storage hoppers and are fed directly to the weighing and mixing room. Minor ingredients are usually stored in their original containers. Cullet (waste glass or rejected ware to be remelted) must be transported to an area where the glass is segregated by type.

Glass batch mixing systems range from full automation to hand operations. Most mixers are of the rotating-barrel type which tumble the batch upon itself in a revolving drum. During a batch mixing process the materials are dry or nearly dry, which causes a loss by dusting. The glass furnace charging may be done manually or automatically, and continuously or intermittently.

Basically, the manufacture of glass is a high-temperature conversion of raw materials into a homogeneous melt for fabrication into useful articles.

There are 3 types of melting units used in the glass industry. Clay "pots" which may be open or covered are used where quantities or special compositions do not justify the use of a tank. This process involves a relatively high proportion of manual handling. The day tank melts batches up to several tons. Finally, most glass is melted in large, direct-fired, regenerative-type furnaces.

Following melting there are several ways to accomplish the forming of glass. The container industry generally is based on modifications of the blowing technique. Glass also may be pressed, cast, rolled, or drawn. Glass fibers can be

made continuously by mechanical drawing, and a glass to be pulverized is dribbled or ladled into water to produce "dry gage" glass.

Final glass operations include finishing and secondary forming operations. Finishing operations may include any one or combinations of the following: flame cut-off, sawing, score and break, score-thermal crack off, thermal crack off, drilling, grinding, polishing, engraving, acid etching, glazing, and sealing. Secondary forming operations may then be used to produce difficult shapes. Before the glass becomes a finished product, a final treatment of tempering or staining may be required.

Although not all glass manufacturers use barium, the information obtained from 8 companies using about 44 percent of the barium indicates the particle size of emissions is less than one micron and the magnitude of emissions is about 2 pounds per ton of barium processed. During 1969 the glass industry used 41,000 tons of barium; therefore, emissions in the United States due to the production of glass totaled about 40 tons during the year.

Paint

Various barium compounds, including barium sulfate, barium carbonate, and lithopone, are used in the manufacture of paint. They are chemically inert and their most important pigment properties are high specific gravity, relatively low oil absorption, easy wettability by oils and vehicles, and easy grinding. They are useful where highly acidic or alkaline conditions are encountered because of their stability toward acids and bases.

Barium sulfate is used to produce several pigments. The lithopone-type cadmium yellow contains from 63 to 66 percent barium sulfate. A medium red shade contains only 59 percent. Lithopone used in the manufacture of white pigment is composed of 70 percent barium sulfate and 30 percent zinc sulfide. Another white pigment is 75 percent barium sulfate and 25 percent anatase titanium dioxide.

Most operations during the manufacture of paints are carried out in closed equipment. Dry pigments, however, are usually received at the plant in bags and there are emissions to the atmosphere that occur: (1) when the bags are unloaded and emptied into storage bins and, (2) when the pigments are added to the mixers.

Although several paint manufacturers contacted during this study indicated they no longer use barium, information was obtained concerning 18 plants that still use it in paint manufacture. Cyclone-type dust collectors are used at 5 plants, bag collectors at 5 others, and there is no emission control equipment at 8 plants. Based on an industry estimate for 8 plants, the barium emissions average 2 pounds per ton of barium processed. During 1969 about 29,000 tons of barium were consumed in paint manufacture and emissions to the atmosphere totaled about 30 tons.

Rubber

Barium sulfate is used as a filler in rubber to improve processing properties and lower the cost of the finished product. It is used along with the raw rubber, accelerators, plasticizers, reinforcing pigments, antioxidants, retarders, and vulcanizing agents. The crude rubber is broken down in the masticating and mixing mill, which consists of two rolls revolving at different speeds with heating and cooling as desired. During the milling operation, carbon black, zinc oxide, sulfur, and other ingredients are added. After milling, the rubber is run through calenders where it is forced into thin sheets and fabric is introduced. Next, the

carcass is formed and the assembled tire is vulcanized at a temperature of 260 to 340 F.

The principal emissions to the atmosphere occur when the finely divided dusts are introduced into the batch at the rubber mills and mixers. Generally, this equipment is provided with hoods to carry away heat generated by the process, as well as particulate and fumes from the rolls.

Information obtained from 3 major producers of vehicle tires and other rubber products shows that cyclone and bag type dust collectors are commonly used for controlling emissions to the atmosphere. Such equipment is not specifically to control barium emissions, but it is located at positions where it is also effective for that purpose. The industry representatives were not able to supply records regarding the magnitude of barium emissions but they provided estimates indicating that the emissions resulting from rubber manufacturing are negligible.

The only significant emissions of barium that occur during the production and use of rubber products appear to be those due to the wear of vehicle tires. Although barium is not used in all tires, the average dosage is in the range of 4 to 5 pounds

per ton of rubber and the average quantity per vehicle tire is about 0.03 pound. During 1969 motor travel in the United States was about 1.05×10^{12} miles including passenger cars, motorcycles, busses, and trucks. The life of a tire averages 20,000 miles and when replaced, 20 percent of the rubber is worn away [1]. Calculated on the basis of 4 tires per vehicle, the barium emissions resulting from the wear of tires during 1969 totaled about 600 tons.

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1 - Private communication.

Miscellaneous

In the United States during 1969 about 129,000 tons (nearly 14 percent) of the barium was used in the form of barite and barium chemicals in processing or as an ingredient in various products including cosmetics, cloth, leather, linoleum, oilcloth, plastics, pharmaceuticals, printers' ink, photographic paper, rat poison, depilitories, pyrotechnics, lubricating oil detergents, water softeners, sugar, and diesel fuel additives.

The information obtained from industry about the use of barium in these end products was valuable in connection with establishing the type of processing operations, the quantity of barium consumed, and the kind of air pollution controls employed; however, only 2 companies provided emission estimates. In general, most processing emission sources with little or no control are those related to materials handling.

One relatively new source of barium emissions to the atmosphere is the rapidly expanding plastics industry. Vinyl stabilizers are used to prevent discoloration during processing and also serve to maintain certain desirable properties during

the useful life of the product. In recent years the number of stabilizers available has increased considerably and those based on combinations of barium, cadmium, and phosphite have become very popular. Although emissions due to the manufacture of barium stabilizers were probably low in 1969, they may become significant in the future.

Numerous compounds that contain heavy metals are marketed as additives for various kinds of oils, including those used for fuel and lubrication. Some for diesel, distillate, and residual oils are used as dispersants, stabilizers, and inhibitors, while others are intended to improve combustion. Those compounds for lubricating oils are principally used as detergents. Additives containing barium also are ingredients in fluids for hydraulic equipment and automatic transmissions. During this study more than 200 additives were examined and 26 were found that contained barium [1]; however, reliable information was not available concerning the actual amount of barium used in additives.

1- "Effects of Fuel Additives on Air Pollutant Emissions from Distillate-Oil-Fired Furnaces"; Environmental Protection Agency; Office of Air Programs Publication No. AP-87, June, 1971.

As stated above, about 129,000 tons of barium were used in the manufacture of various products. Emission data available from industry were limited. Based on the type of processing operations and air pollution controls employed, the Contractor's estimate of barium emissions for the year 1969 is 3,500 tons. It is likely this estimate is low; it is reasonably certain that it is not high by more than 30 percent.

SOURCES OF INADVERTENT BARIUM EMISSIONS

COAL

A search has been conducted and information has been found regarding the barium content of coal, ash of coal, and fly ash emissions from coal fired power plants.

With respect to fly ash, there is a study of emissions from coal fired power plants that has been made which shows the analysis of several fly ash samples. Six power boilers were tested, each a different type, and each value reported was the average of at least 2 tests. Two of the boilers were fired with Illinois coal; 2 burned Pennsylvania coal; one used some coal from Ohio and some from West Virginia; one burned part Kentucky and part West Virginia coal. The coal burned during the tests represented only a small portion of the coal mined in the various regions of the United States.

Barium concentrations in the fly ash samples taken before fly ash collection ranged from 3.65 to 27.2 x 10^{-4} grains per scf [1]. The average was 14.5 x 10^{-4} grains per scf.

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1. Cuffe, Stanley T. and Gerstle, Richard W.; "Emissions from Coal Fired Power Plants"; Public Health Service Publication No. 999-AP-35; 1967.

Calculations have been made based on:

(a) 516,084,000 tons of bituminous and anthracite coal consumed in the United States during 1969 [1];

(b) 160 scf of flue gas per pound of coal;

(c) 14.5×10^{-4} grains per scf barium concentration;

(d) 85 percent efficiency of control; and

(e) 90 percent application of control.

The barium emissions calculated in this manner totaled 4,000 tons.

$$\frac{516,084,000 \times 160 \times 14.5 \times 10^{-4} \times 2,000}{7,000 \times 2,000} \left[1 - (0.85 \times 0.90)\right] = 4,000$$

During the combustion of coal, barium is discharged with the ash part with the bottom ash and part with the fly ash. The fly ash averages about 65 percent of the total ash.

Many samples of coal have been analyzed and the barium content reported as shown in Table IV. Calculations have been made based on:

(a) 516,084,000 tons of bituminous and anthracite coal consumed in the United States during 1969 [1];

1- Minerals Yearbook. Bureau of Mines. 1969.

(b) 89 ppm average barium concentration in coal;

(c) fly ash 65 percent of total ash;

(d) 85 percent efficiency of control; and

(e) 90 percent application of control.

The barium emissions calculated in this manner totaled 7,000 tons.

$$516,084,000 \times 89 \times 10^{-6} \times 0.65 \left[1 - (0.85 \times 0.90)\right] = 7,000$$

In this report the figure of 4,000 tons is used as the barium emissions to the atmosphere during 1969 due to the combustion of coal.

TABLE IV

AVERAGE BARIUM CONTENT IN ASH OF COAL

Region	Frequency of Detection - %	Ba Content of Ash - %	Ash Content of Coal - %	Ba Content of Coal - %
Eastern Province	100	0.0876	9.3	0.0081
Interior Province	100	0.0399	10.5	0.0042
Western States	100	0.1467	9.8	0.0143
Average Barium Content of Coal				0.0089

NOTE - The above table based on "Spectrochemical Analyses of Coal Ash for Trace Elements", Bureau of Mines RI 7281; Table 1; July 1969.

OIL

In order to estimate barium emissions to the atmosphere due to the combustion of fuel oil, it is necessary to determine the barium content and the quantity of oil received from numerous foreign and domestic sources. Information was located showing the analyses of more than 100 samples of domestic crude; however, the situation was different with respect to residual oils and foreign crude. The only reliable information available on residual oil was that regarding nickel and vanadium.

Due to the lack of reliable data, there is no estimate of emissions set forth in this report other than a suggested range of values. Based on the Contractor's studies of other metal emissions due to the burning of fuel oil, barium emissions should range between 100 and 1,000 tons for the year 1969.

IRON AND STEEL

During this study spectrographic analyses of dust samples from 3 iron foundries have been examined and they show barium is present in all samples, the content ranging from 0.01 to 0.07 percent [1].

The cupola is the most popular method for producing cast iron and the rate of particulate emissions from gray iron cupolas has been reported as 4 to 26 pounds per ton of process weight not including emissions from materials handling, charging, or other non-melting operations.

Based on information obtained from industry the particulate emission factor is estimated at 22 pounds per ton of process weight, including melting and non-melting operations. The degree of emission control is approximately 25 percent. Calculations show that with 0.03 percent barium in the particulate, the emission factor is 0.005 pound of barium per ton of process weight.

During 1969 the pig iron and scrap used by iron foundries

1- Private communication.

totaled 18,594,000 tons [1]; therefore, barium emissions to the atmosphere due to the production of cast iron were 50 tons.

There was some information located during research that indicated barium as a trace element in the discharge from an open-hearth furnace [2] but no data was obtained regarding blast, electric, or basic oxygen furnaces. The emissions of barium to the atmosphere during steel production are estimated to be less than 200 tons for 1969.

1- Minerals Yearbook: Bureau of Mines; 1969.

2- "Air Pollution Engineering Manual"; Public Health Service Publication No. 999-AP-40; p. 243. 1967.

UPDATING OF EMISSION ESTIMATES

The emissions and emission factors presented in this report are the result of calculations based principally on information obtained from industrial sources. They are specifically for the year 1969, but may be updated at any time when additional information is available. Either of the 2 methods described herein may be used for updating; however, the longer procedure, referred to as Method A, will yield results that are much more reliable.

The procedures to be followed with Method A are essentially the same as those used during the original study, which are described briefly as follows. More than 150 inquiries were sent to processing and reprocessing companies by mail or delivered during personal visits to plant sites. There was no reply from 56 companies. Another 59 companies answered but did not provide data. There were 37 companies that furnished all or part of the data requested and that information was the basis for emission factors and emission estimates set forth in this report.

All of the companies that produce barite were requested to provide the essential data required for the study. Information

was obtained concerning 10 of the 19 mining operations in Arkansas, Georgia, Missouri, and Nevada. The chemical producing companies and manufacturers of end products that provided information represented about 40 percent of the industry capacity.

Regardless of the method selected, the first step to be taken when updating the emission estimates is to obtain the latest issue of the Bureau of Mines Minerals Yearbook, Volume I-II, which is normally available within 16 to 18 months after the end of the calendar year (preprints of individual sections are usually available sooner). This publication shows the quantity of barite sold or used by producers, as well as the quantity imported. It also shows the amount of barite sold by producers for use in well drilling, barium chemicals, glass, paint, and other uses. In this one publication most of the information is available that is required to update the material flow chart for barium. Additional information may be obtained from the commodities specialists at the U. S. Bureau of Mines.

When using Method A, the emission factors must be revised by contacting industry to determine the improvements in air

pollution collection equipment efficiency and other processing changes affecting barium emissions. The revised emission factors may then be used with the production quantities obtained from the Minerals Yearbook or other referenced sources.

Method B is considerably shorter than Method A and less reliable. The only requirement is to revise the material flow chart according to the most recent published data and apply the emission factors shown in this report. In reality this method is only a partial updating. There is no determination regarding improvements in air pollution control, a shift in production to more efficient plants, or any other considerations affecting emission factors. The advantage is that the report can be updated within a few days, rather than several months.

To update barium emissions from processing, chemical production, beet sugar refining, plastics, and petroleum additives, it is preferable to use Method A. The remaining emissions shown in this report may be updated by Method B without introducing an appreciable error into the results.